NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Silicon Electrolyte Interface Stabilization (SEISta): Advanced Characterization

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National Renewable Energy Laboratory

6/2/2020

Project ID # **bat438**

NREL | Sandia National Laboratories | Berkeley Lab | Oak Ridge National Laboratory | Argonne National Laboratory | Pacific Northwest National Laboratory

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Overview

Timeline

- October 1st 2016 - September 30st 2019.
- Percent complete: 60%

Budget

- Funding for FY20: $3800K

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  - Cost, Performance and Safety

Partners

- Six Laboratory Team lead by NREL:
  - Sandia National Laboratory
  - Argonne National Laboratory
  - Oak Ridge National Laboratory
  - Lawrence Berkeley National Laboratory
  - Pacific Northwest National Laboratory
- UC Berkeley, Colorado University Boulder, Colorado School of Mines, University of Rhode Island

Program Relevance

Si anodes are ~10x higher capacity than graphite anodes

1. Si anodes have three major challenges to commercialization
   - High Capacity Fade
   - Poor Shelf Life
   - Electrode formulation/stability
2. SEI formation in Si much more complex than in graphite, and seems to be dependent on initial state and history
   - Large volume expansion on alloying
   - Extensive gas formation upon

Objective:

Improve calendar life and understand initial stages of SEI formation by understanding intrinsic chemical reactivity of Si electrodes

FY20 Milestones

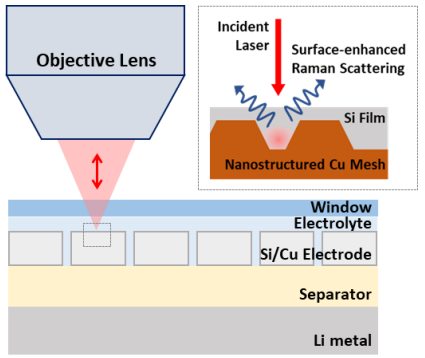
1. Have demonstrated ability to make model electrodes of Mg-Si zintl compounds and compared SEI chemistry to silicon using XPS, STEM-EDS and FTIR/Raman. **Q1 Complete**
2. Have established experiments and protocols for understanding the factors that affect safety in silicon anodes, with a specific focus on highly exothermic reactions that occur at silicon electrodes. **Q1 Complete**
3. Have determined the affect that CO2 has on the stability of SEI formation on model electrodes, but examining the changes in the nature of the SEI (XPS, and FTIR/Raman and quantitate electrochemical measurement) as a function of CO2 concentration. **Q2 Complete**
4. Have determined zintl phase formation mechanism and its effect on SEI with model systems including Si NPs, Si wafer, a-Si thin film using XPS, AFM/SSRM, STEM-EDS and FTIR/Raman. **Q2 Complete**
5. **Go/NoGo** on production of tin-silicon alloys to be determined by the ability of the alloys to be prepared in 1g quantities and a demonstration that the alloys exhibit greater cyclic life than the pure metals alone. **Q2 Complete**
6. Have determined the chemistry and interfacial properties (e.g. nature of the chemical bonding at the surface of Si and the organic material) of LiPAA/Si interfaces as a function of charge (OCV, 0.8V, 0.4V, 0.15V, 0.05V) and drying temperature (100, 125, 150, 175, 200C). **Q3**
7. Have determined how binder changes the stress/strain on silicon electrodes as a function of state of charge by varying Si NP size and surface functionally utilizing both 2D and 3D model systems. **Q3**
8. Have implemented protocols that enable comparisons of safety responses in silicon anodes as a metric for improving safety in silicon cells. **Q3**
9. Have published a document that will enable other research and development groups to analyze stability of the SEI on a silicon-based anode, thus enabling developers or researchers to continually improve silicon cell stability (joint milestone with the Silicon Deep Dive). **Q4**
10. Have understood how the nature and amount of formed/soluble SEI species varies with electrolyte, binder, and Si anode (with surface functionalization) using GC-MS, (in-situ) FTIR/Raman and XPS. **Q4**

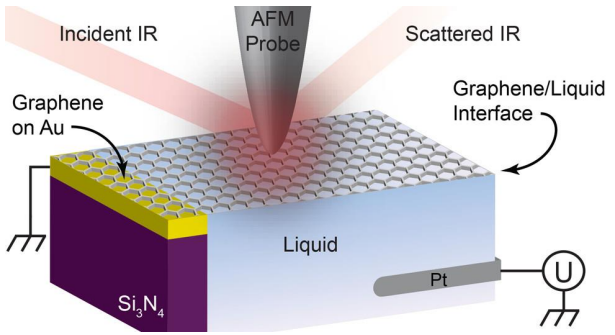
The SEISta team develops and applies advanced characterization approaches that facilitate progress on milestones.

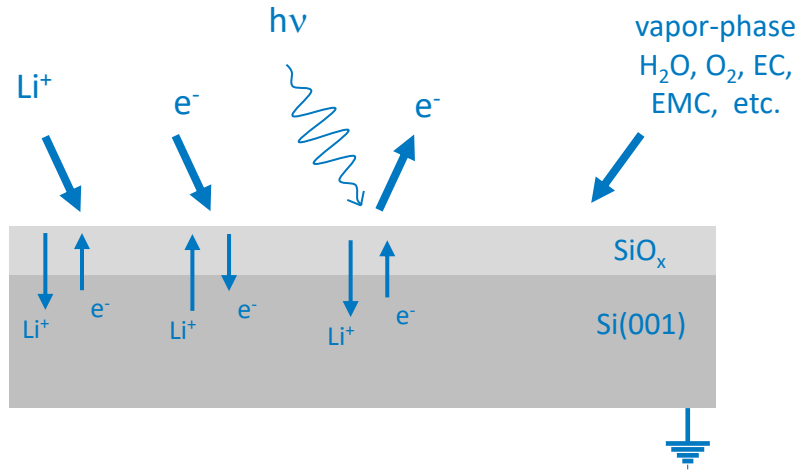
Approach: Focus on *in situ* and *operando* characterization approaches

Develop and Apply novel Characterization Approaches to Study SEI Processes:

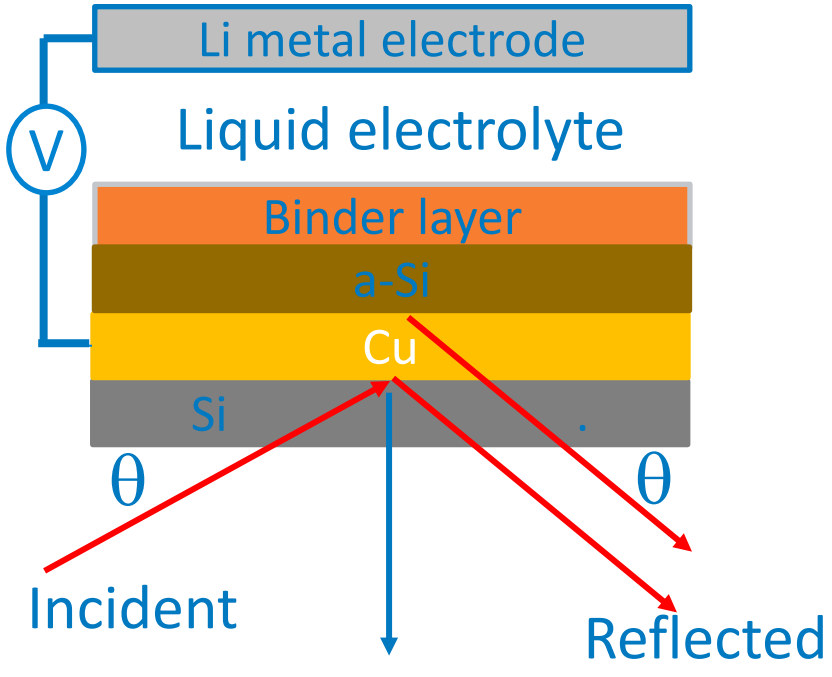
- *In situ* Neutron Reflectometry
- *In situ* Surface-Enhanced Raman Spectroscopy
- MALDI coupled with on-electrode Chromatography
- *in situ* Near-Field FTIR and AFM
- Scanning Spreading Resistance Microscopy (SSRM)
- ”virtual-electrode” *operando* XPS

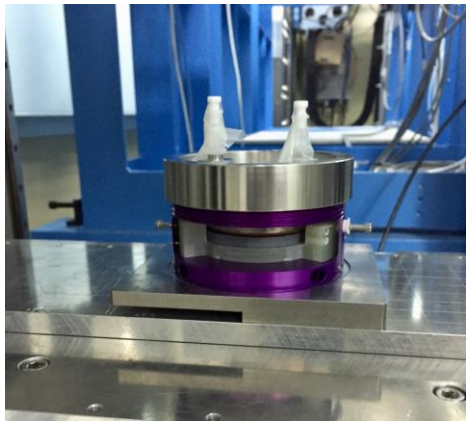




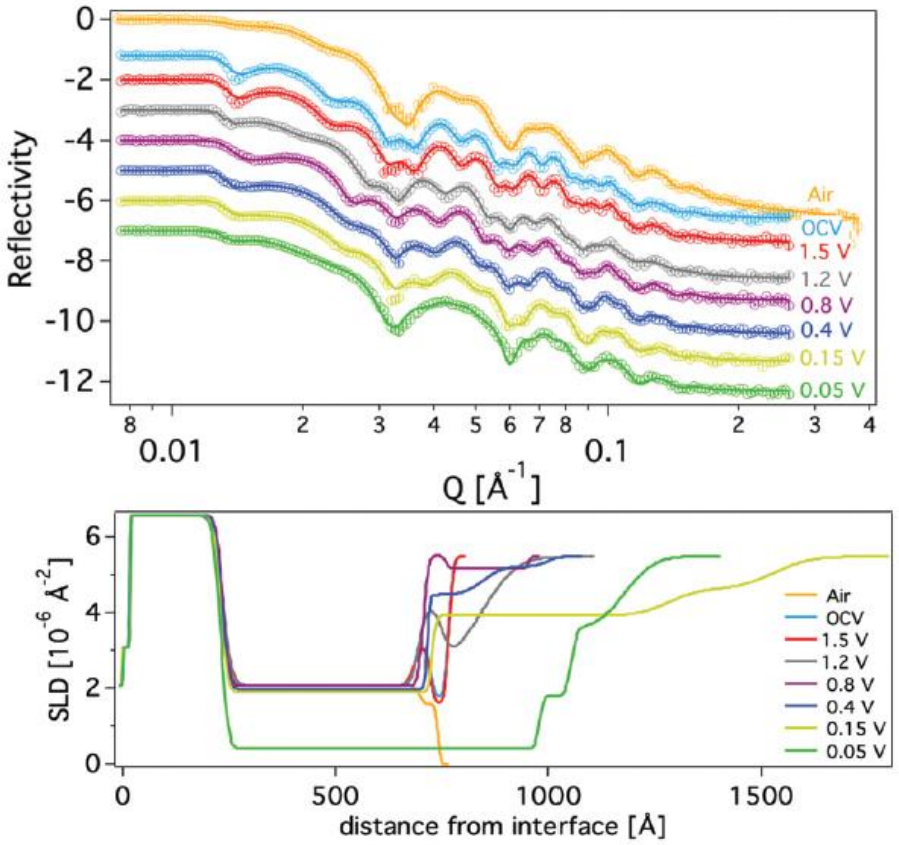


In situ neutron reflectometry probes SEI chemistry as a function of charge and binder chemistry





- Used to measure thickness and composition with time and state-of-charge *in situ.*
- Sensitive to Li and H

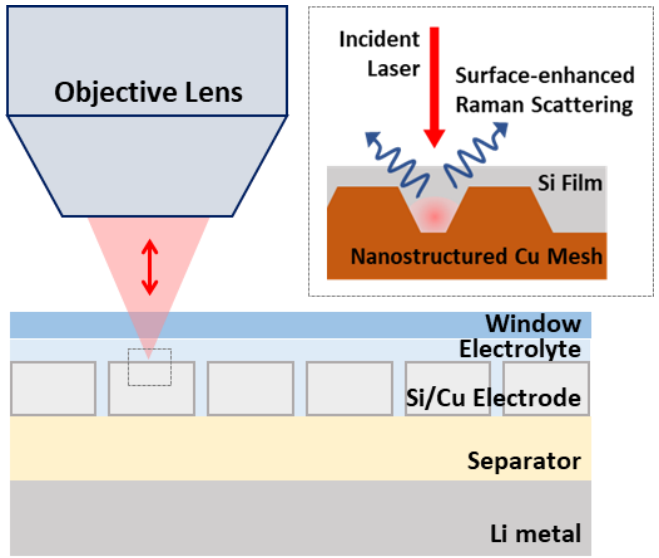


See multiple changes in film structures associated with SEI and Si evolution

Fits to the data show changes in composition and thickness

Novel Characterization Technique: *in situ* Raman Spectroscopy

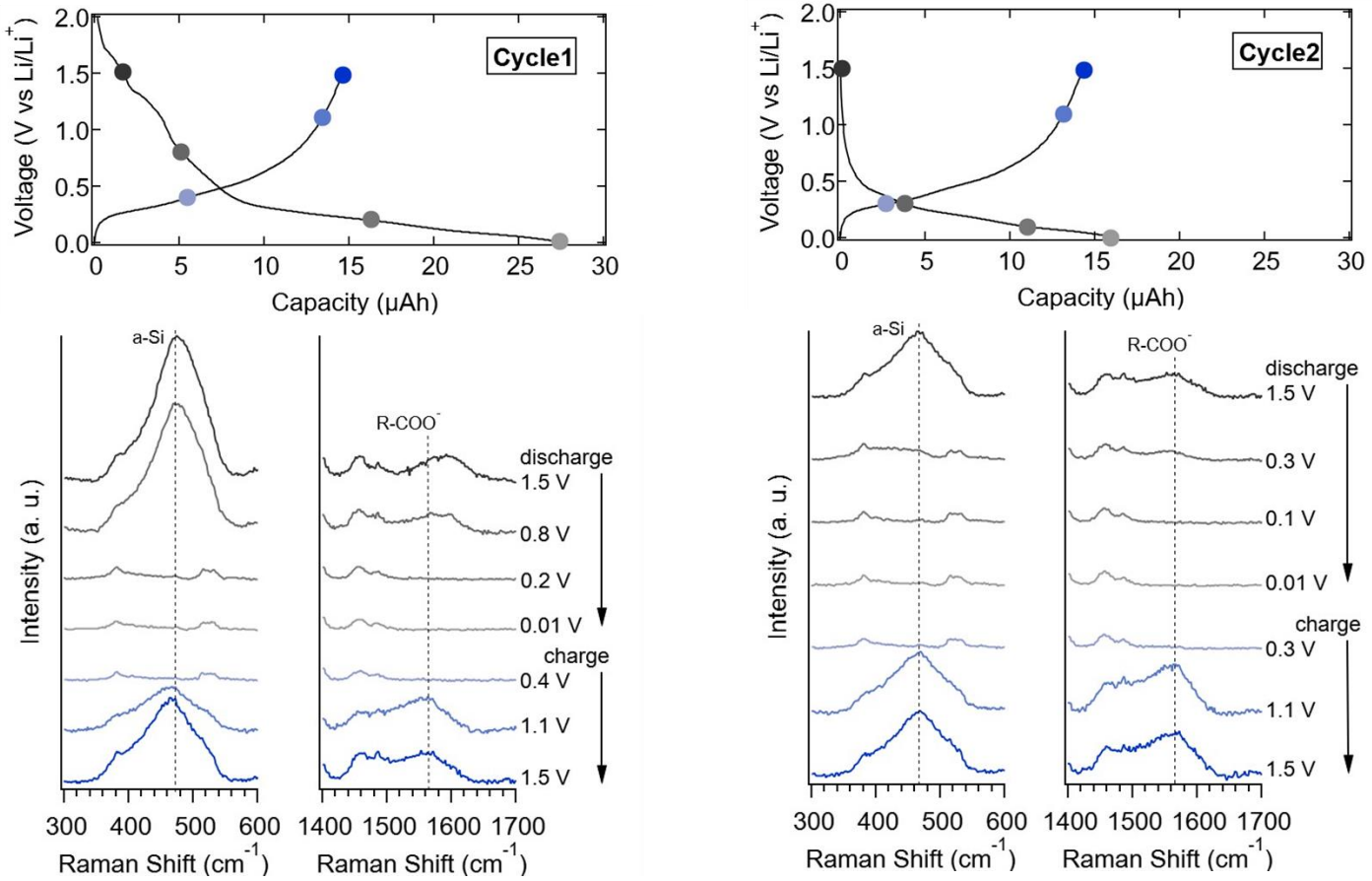
Surface-enhanced Raman Spectroscopy (SERS)



- Have utilized SERS to monitor the evolution of the silicon–electrolyte interphase (SiEI).
- Have showed reproducible and stable performance over multiple cycles in terms of both electrochemistry and spectroscopy.
- Can be applicable to other battery systems and the electrode–electrolyte interphase contained within.

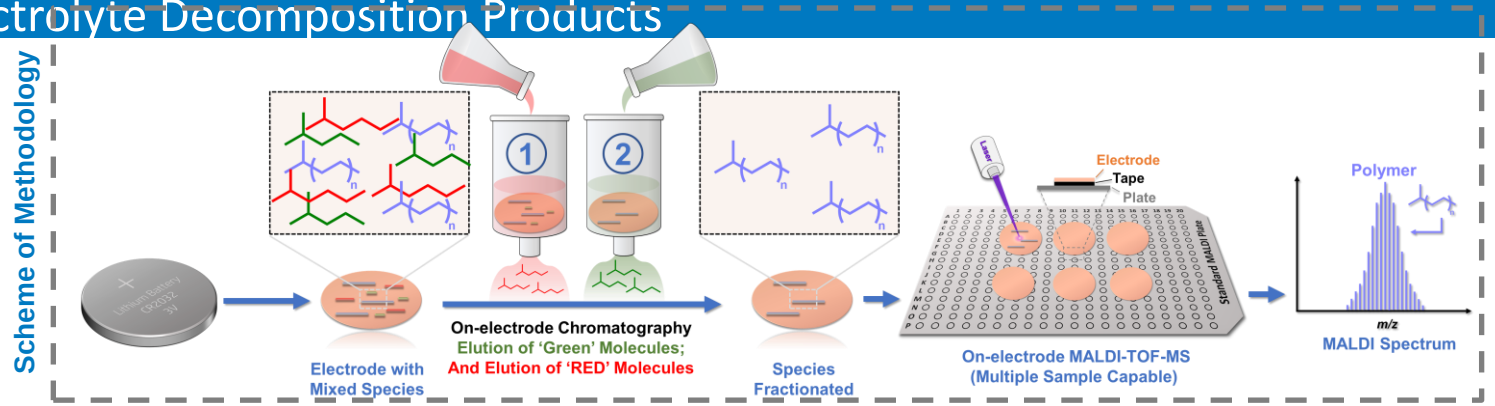
Y. Ha *et al., J. Phys. Chem. Lett.* **2020**, *11*, 286.

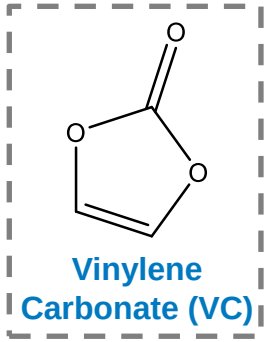
Galvanostatic Cycling Voltage Profiles and Corresponding *in situ* SERS spectra

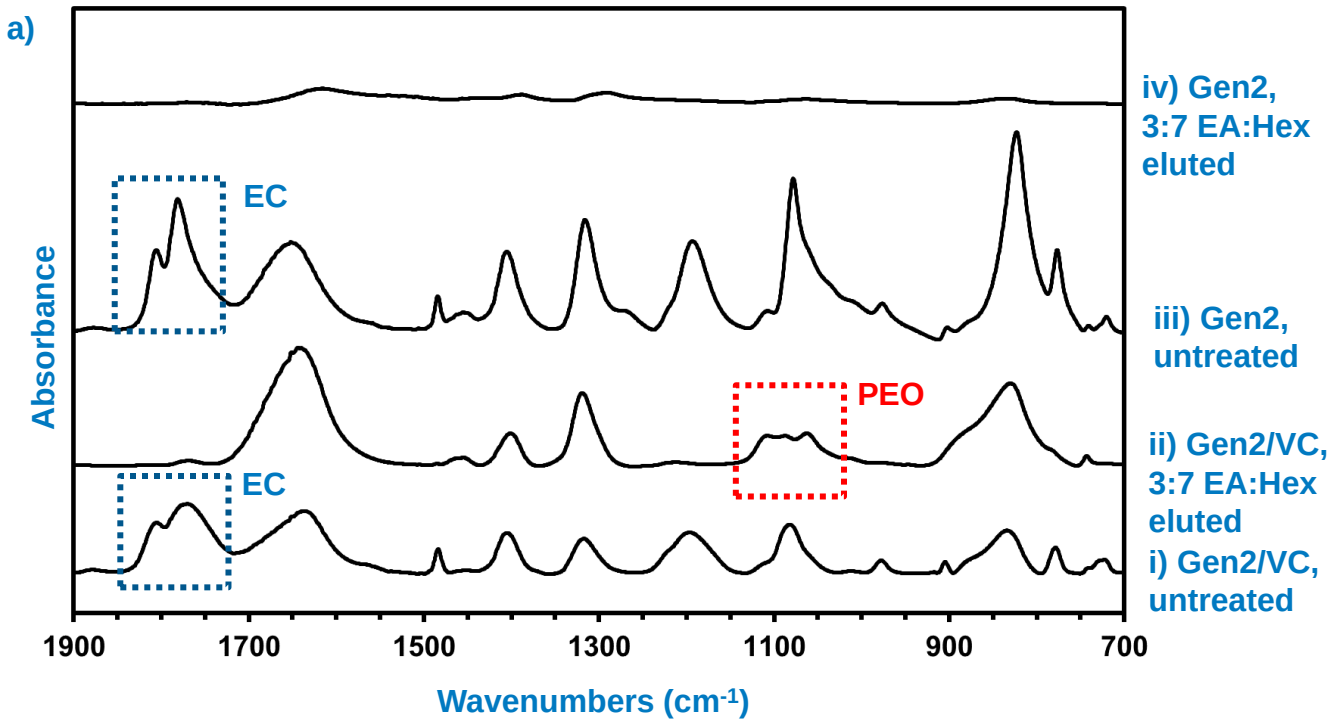


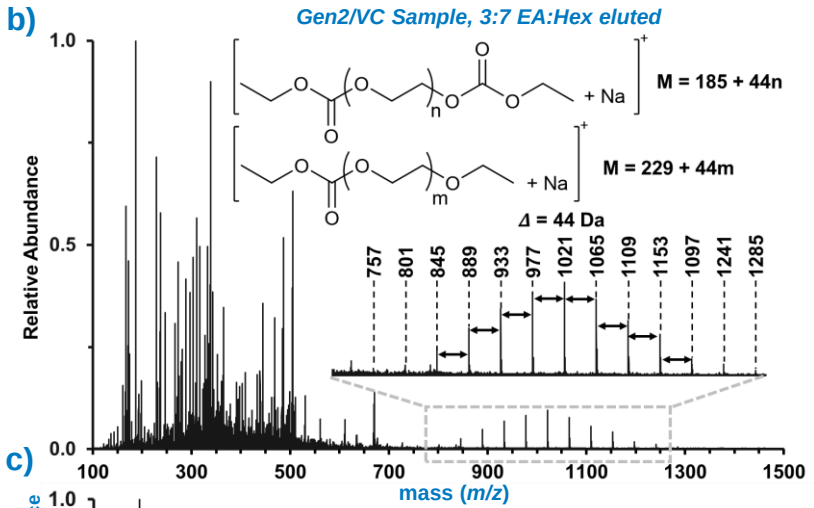
- Amorphous Si thin film electrode cycled in a Gen2 electrolyte at 15 μA within 0.01-1.5 V (*vs* Li/Li$^+$)
- Reversible peak changes corresponding to the amorphous Si (a-Si, 470 cm^{-1}) and alkyl carboxylate species (R-COO$^-$, 1565 cm^{-1}) as one of SiEI components

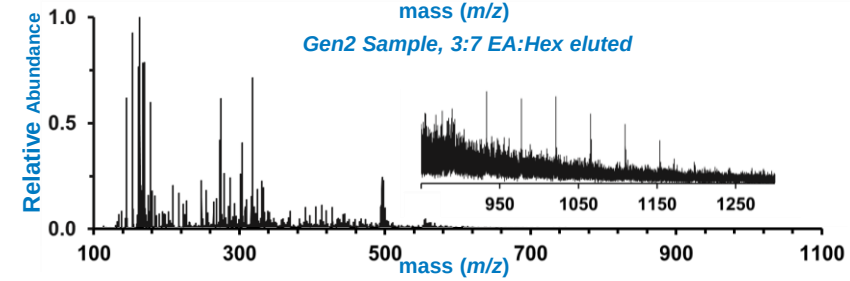
Complementary MALDI-TOF-MS and On-electrode Chromatography for Identification of Electrolyte Decomposition Products











Possible PEO Structures

VC Promotes high-mass PEO formation

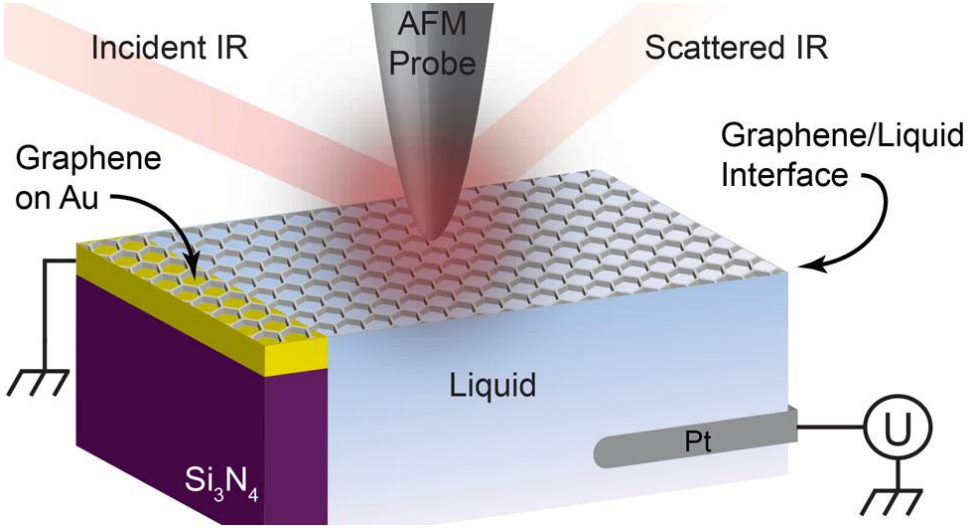
PEO formation minor without VC

a) FTIR spectra of untreated and treated (by 3:7 EA:Hex) electrodes cycled with and without VC additive (Gen2 electrolyte: EC:EMC 3:7 w/w, 1.2M $LiPF_6$). MALDI spectra of electrodes cycled with b) Gen2/VC after 3:7 EA:Hex treatment and c) Gen2 after 3:7 EA:Hex treatment (inserts are zoom-in spectra of PEO regions and proposed PEO structures).

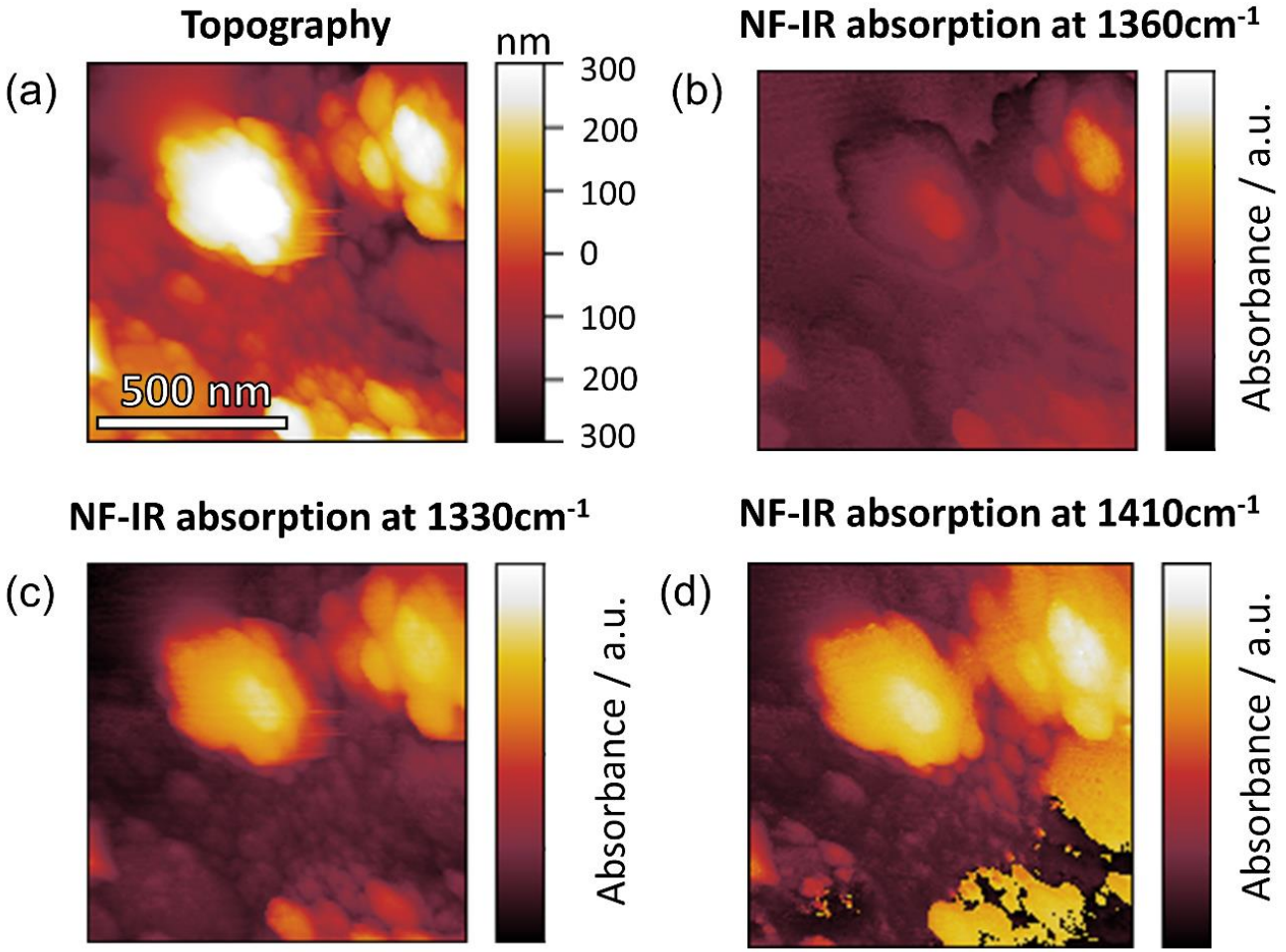
Optical Spectroscopy and Microscopy of Si/Electrolyte Interface

High surface resolution near-field FTIR probe

- Coupling electrochemical measurements with optical scanning nanoprobes.
- Adapt infrared nano-spectroscopy and microscopy to investigate Si/electrolyte interface at nm resolution.



Kostecki et al., Nano Lett. 2019



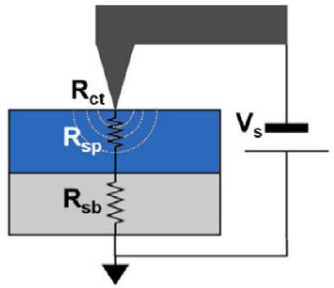
Near-field FTIR 1 x 1µm images of a-Si-TF electrode at 0.05 V

AFM & SSRM: Heterogeneous Lithiation Behavior on SiO_2-coated Si Wafers

Technique: SSRM Resistivity vs. Depth Profiling

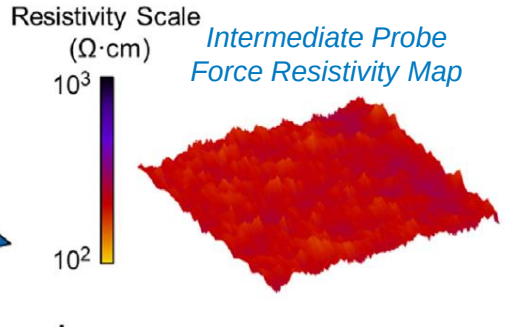
- Electronic resistivity of SEI mapped with nm-resolution by SSRM with a logarithmic amplifier within a range of 10^{-2} – 10^{11} Ω·cm
- Resistivity vs. depth profiles developed by mechanically milling away material with the probe, exposing structures beneath

Instrument Schematic

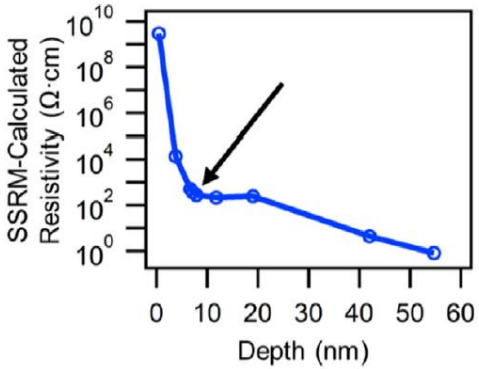


Concept

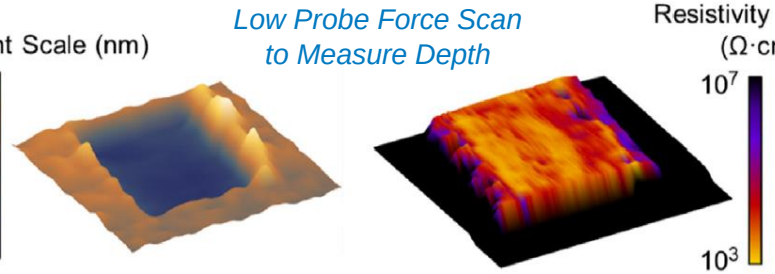
Intermediate Probe Force Resistivity Map



Resistivity vs. Depth Profile

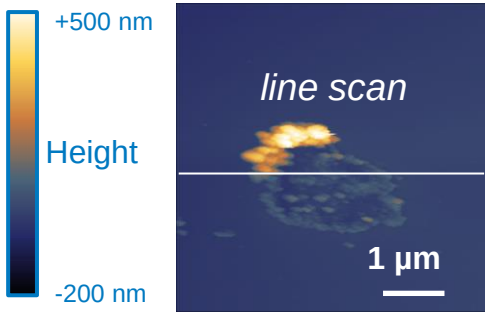


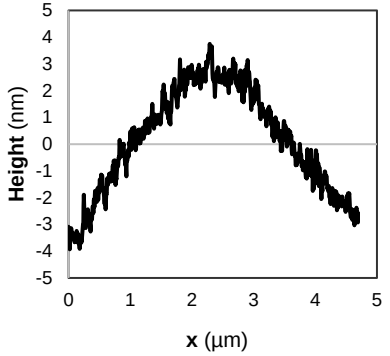
Low Probe Force Scan to Measure Depth



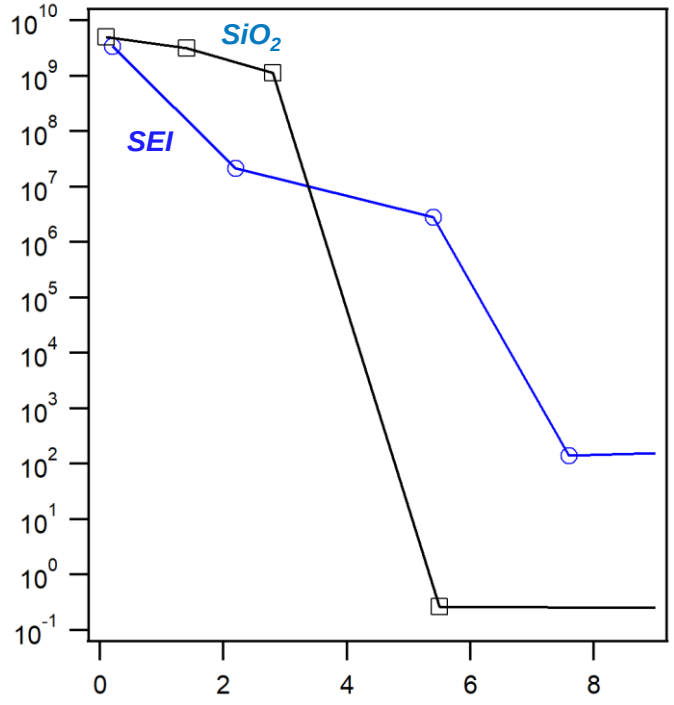
C. Stetson et al., *Nano Energy 55, 477(* 2019).

AFM Morphology



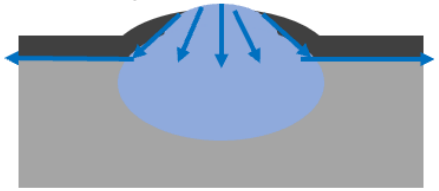


SSRM Resistivity Depth Profiles

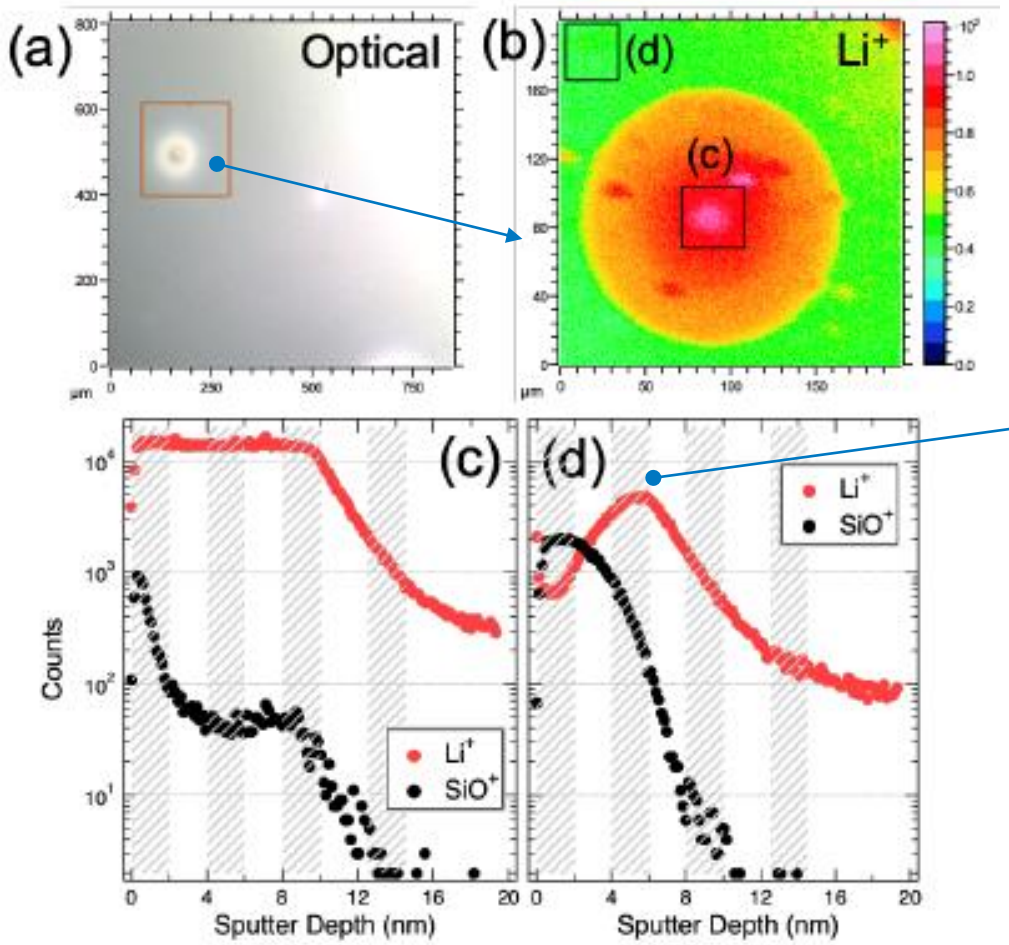


- **Swelling in vicinity of central pinhole feature and local SEI accumulation identified by AFM**
- **Within feature, SSRM shows SEI formation, disruption of SiO_2, and an increased electronic resistivity of the underlying Si consistent with cycling**
- **Outside feature, SiO_2 is intact**

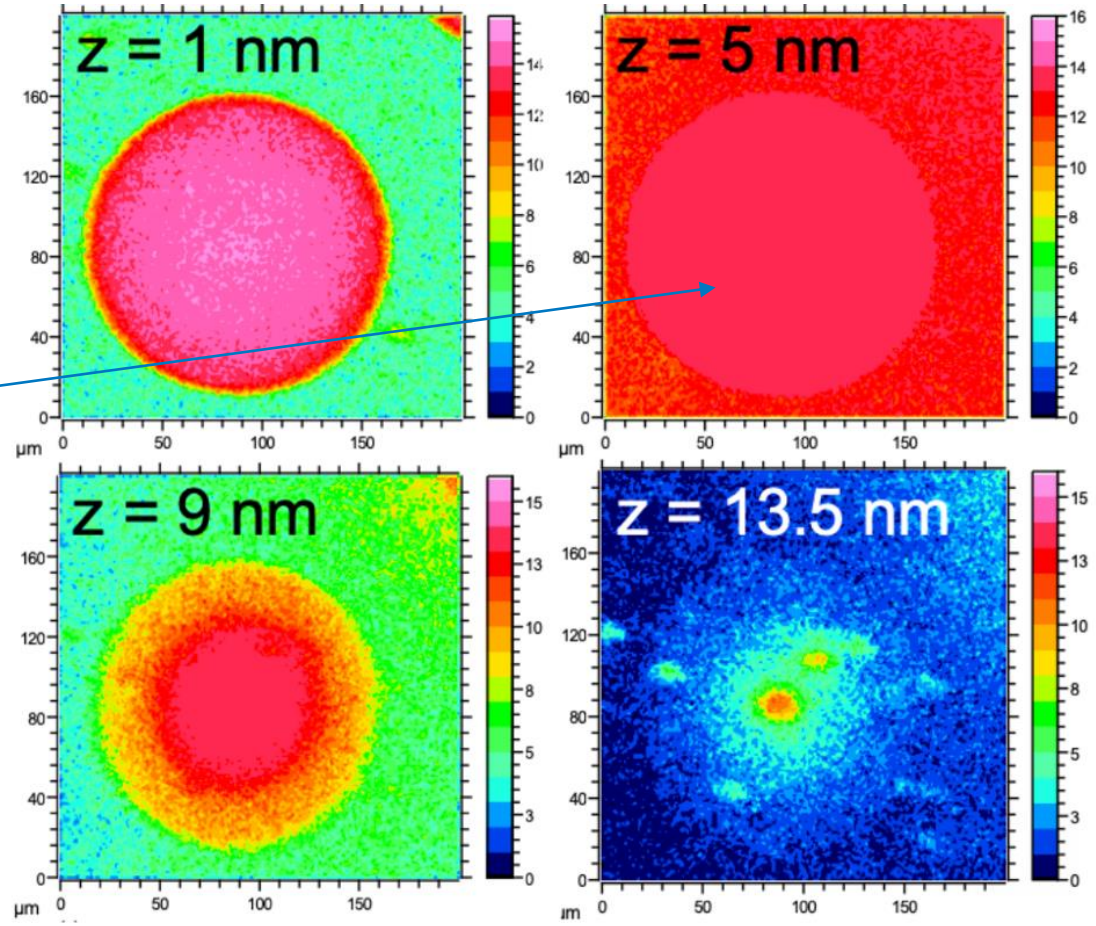
Breakage of local SiO_2 at vicinity of original pinhole, due to weakening of the film by local expansion-contraction



TOF-SIMS Measurements on lithiated 5-nm SiO_2/Si(001)



Schnabel et al., ACS Mater. Interfaces (2020, submitted)

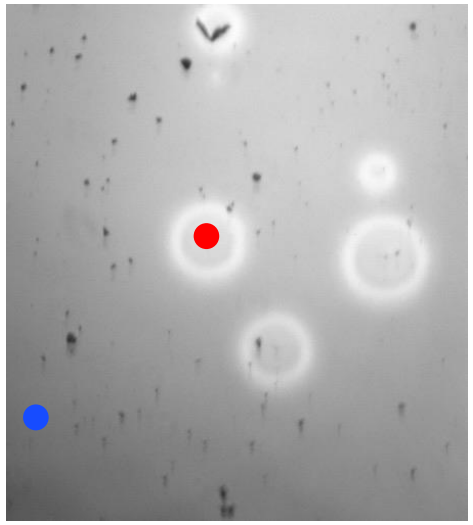


TOF-SIMS: Li^+ signal at distinct depths

- Li_xSi region corresponds to disk-like feature observed in optical-contrast images
- Li also accumulates at SiO_2/Si(001)interface > 130 microns from the pinhole.

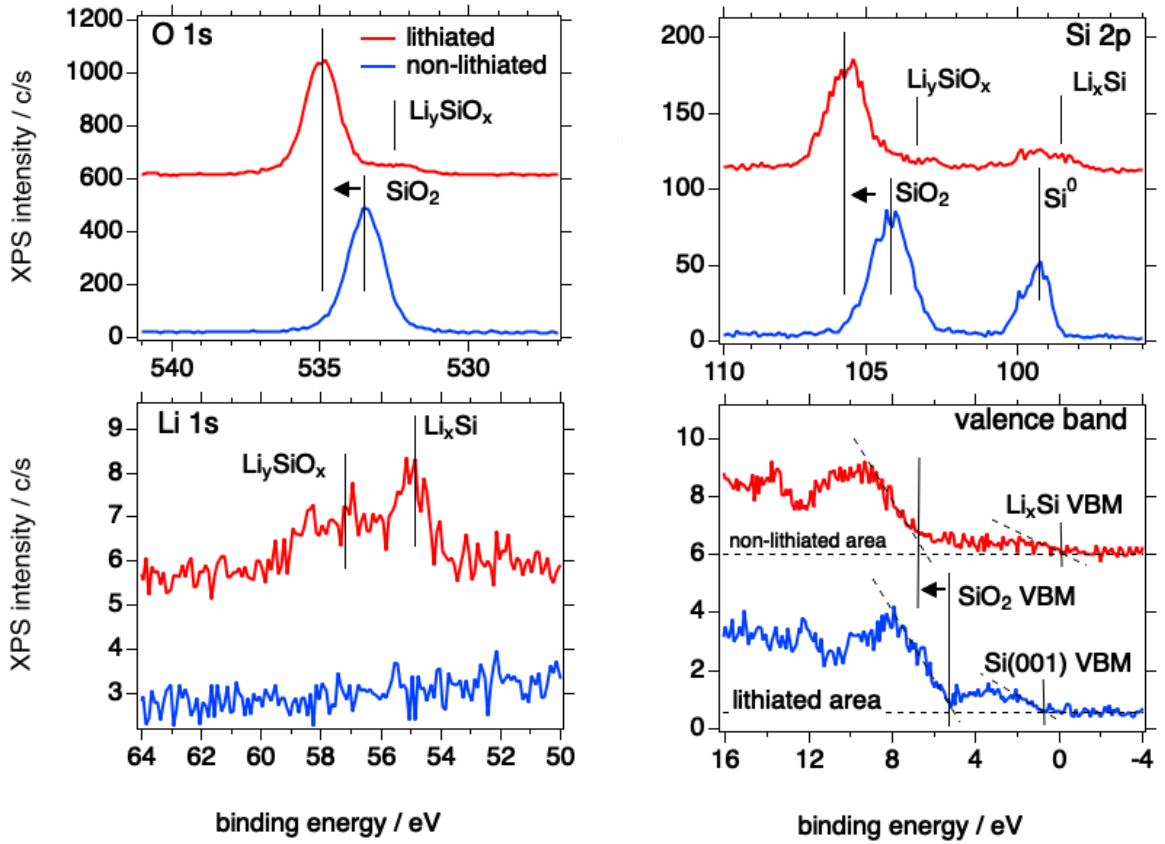
Lithiated 5-nm SiO_2/Si(001) wafer anode sample: small-spot XPS analysis

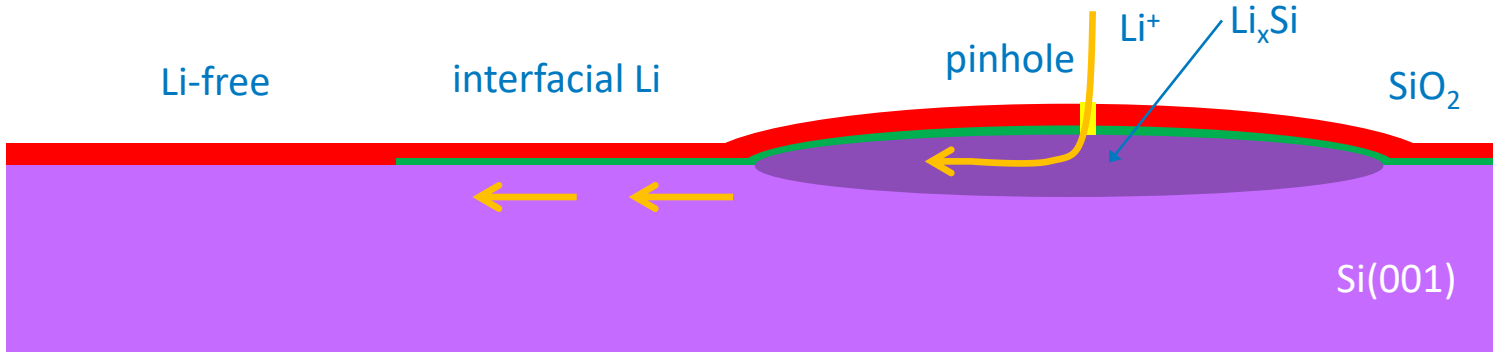
optical micrograph



5-nm SiO_2/Si(001) wafer anode

- electrochemically lithiated
- lithiated spots form—possibly due to pinholes in SiO_2
- small-spot XPS spectra were acquired on and off lithiated spots
- XPS core-level shifts are consistent with previously observed shift in SiO_2/Si(001) caused by Li^+ exposure

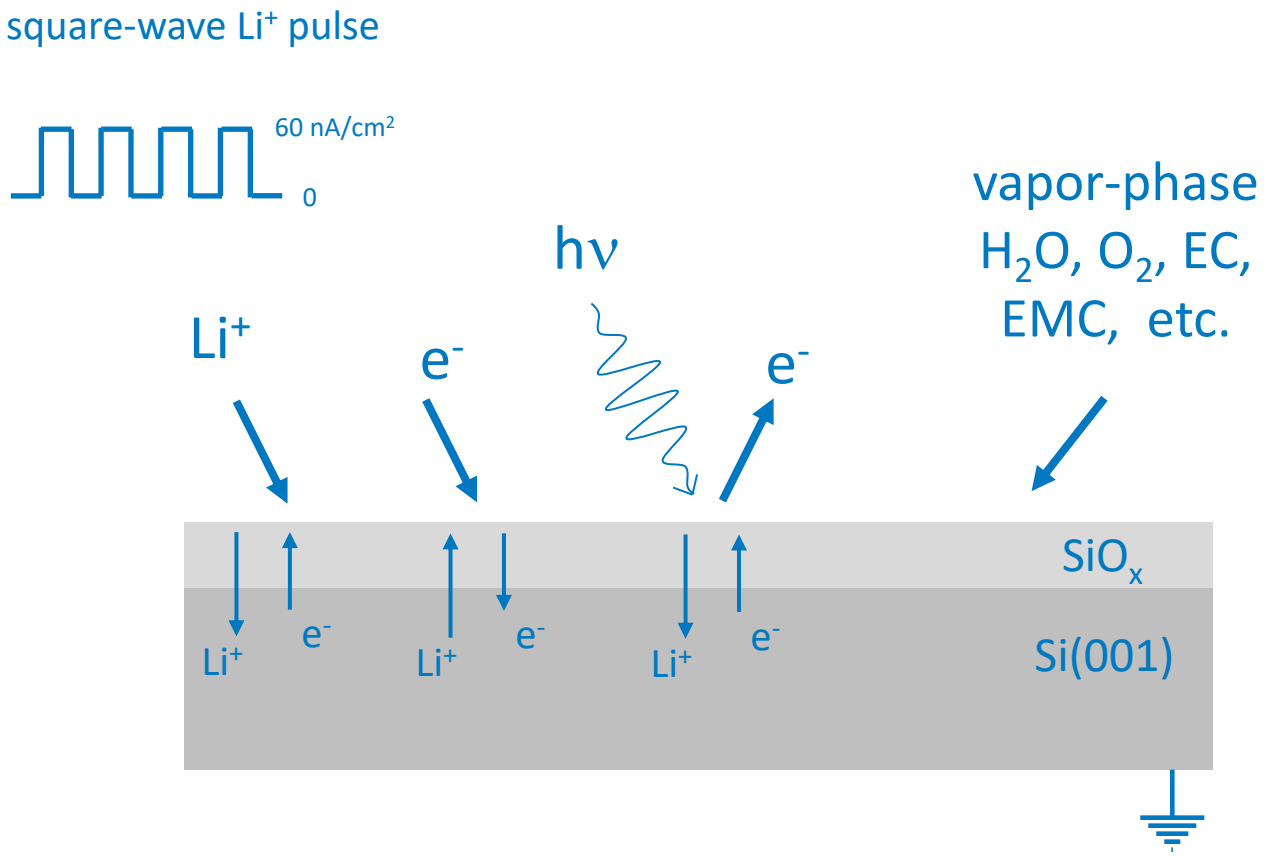




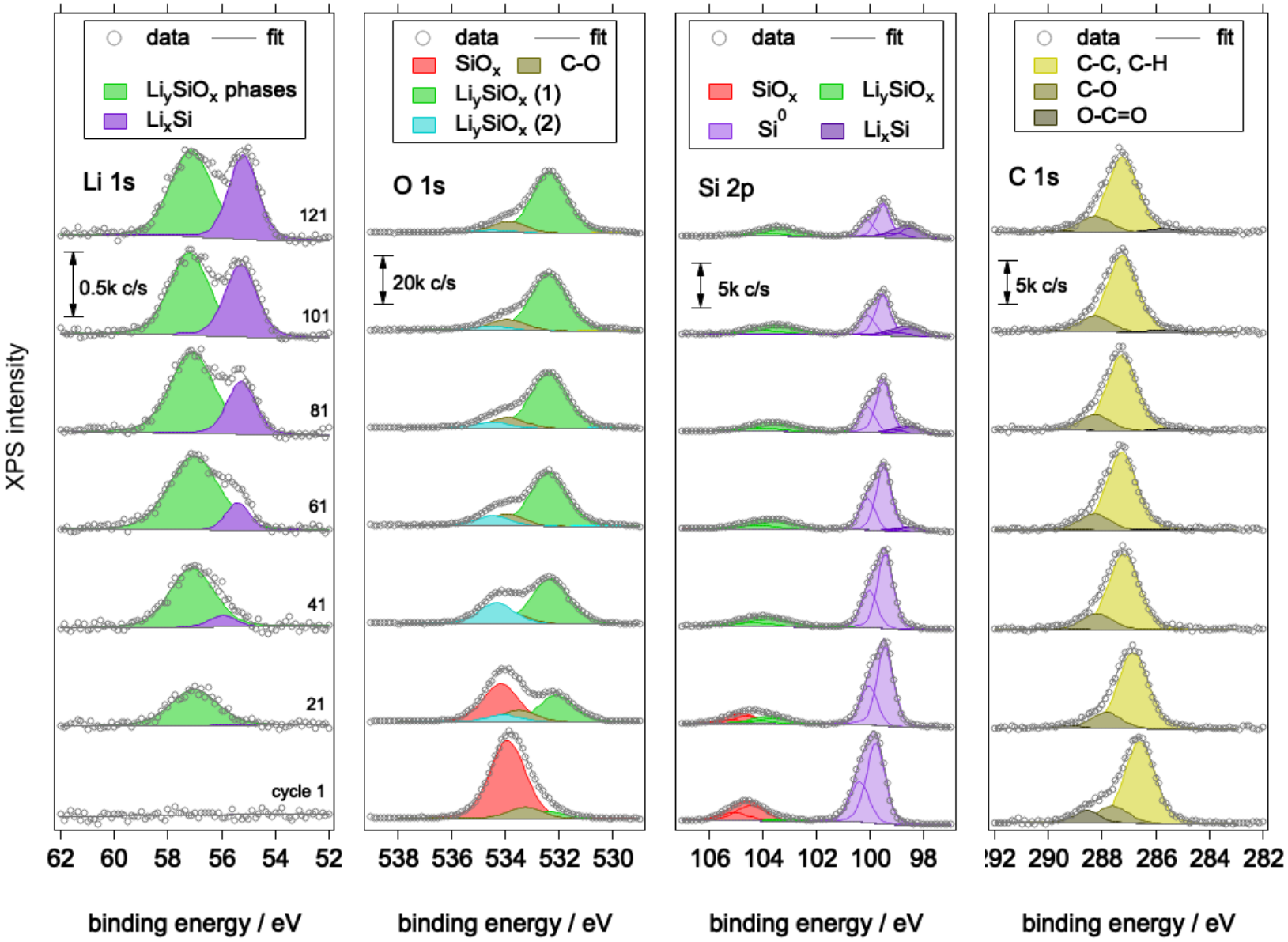
XPS *in-situ* lithiation and related experiments

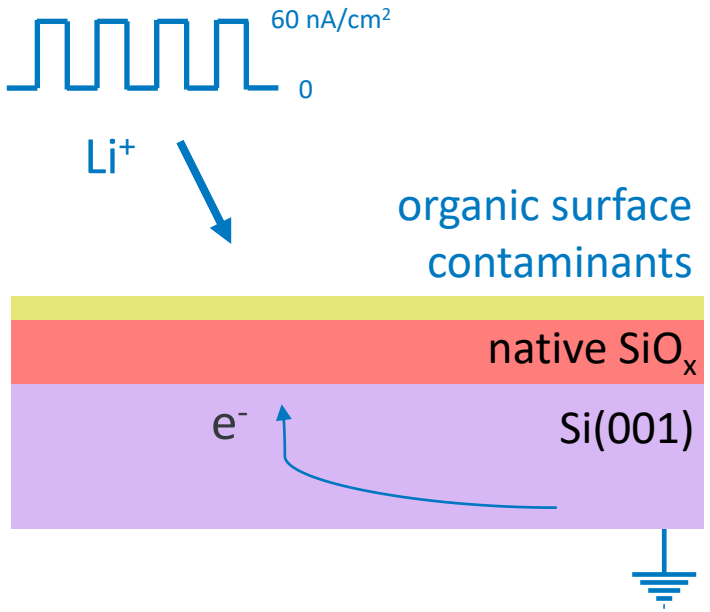
Virtual electrode approach

- Li^+ ion gun
  - 1–1000 eV incident energies
  - isotopically enriched ^6Li cathode
  - typical current densities ~200-500 nA/cm^2
  - raster and pulsing capabilities
- e^- gun
  - 1–1000 eV incident energies
  - typical current densities ~1-5 μA/cm^2
  - raster and pulsing capabilities
- light sources
  - 365 – 850 nm high-power LEDs (CW-500 kHz)
  - 670 nm laser diode (CW-100 MHz)
  - can drive photoelectron current (ϕ < 3 eV)



XPS *in-situ* lithiation of native SiO_x/Si(001)





XPS in situ lithiation:

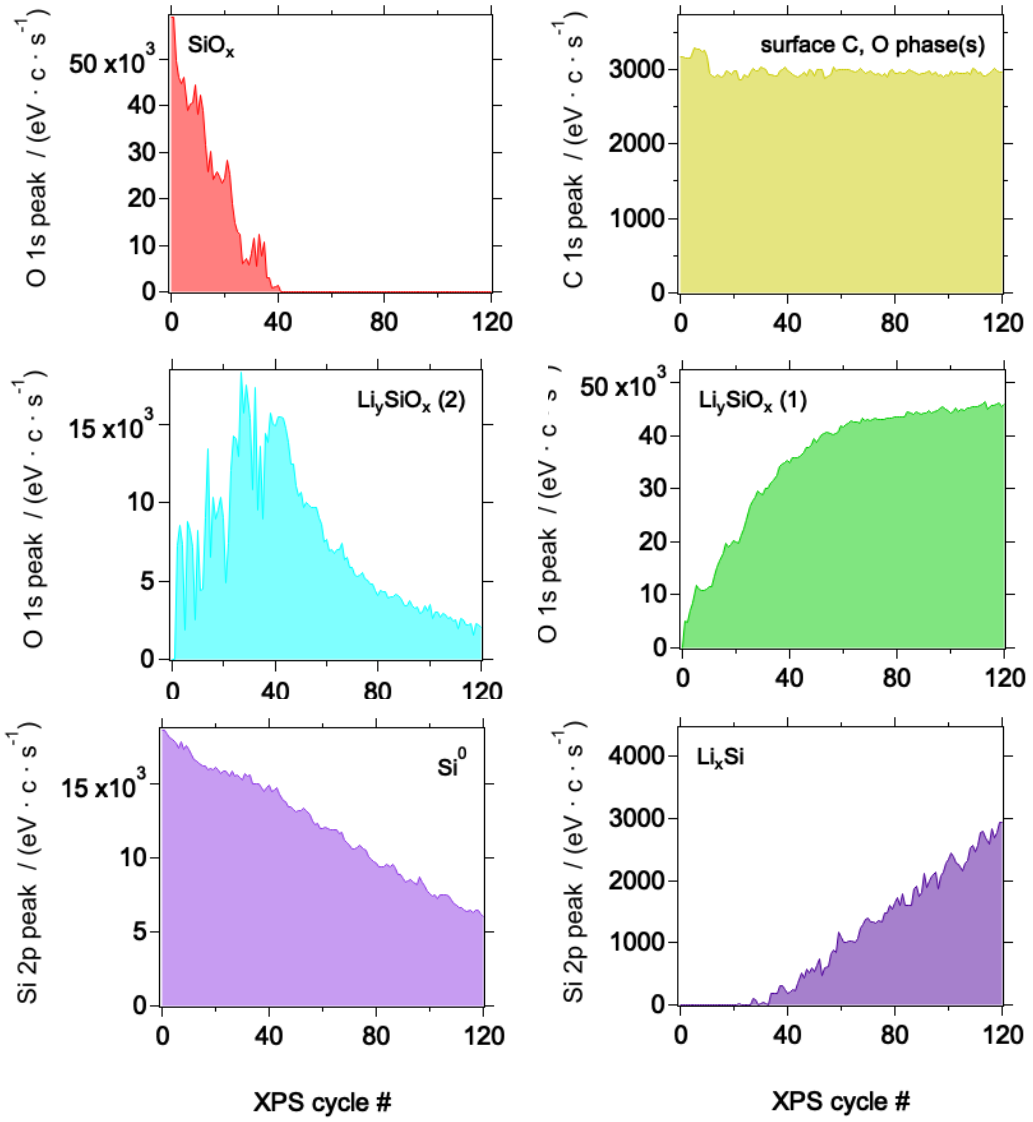
- native SiO_x/Si(001) model-system anode
- Li^+ ion gun (60 nA/cm²) was pulsed to reveal changes in overpotential
- Chemical-state changes reveal sequential formation of Li_ySiO_x and Li_xSi phases:

$$SiO_x + yLi^+ + e^- \rightarrow Li_ySiO_x$$

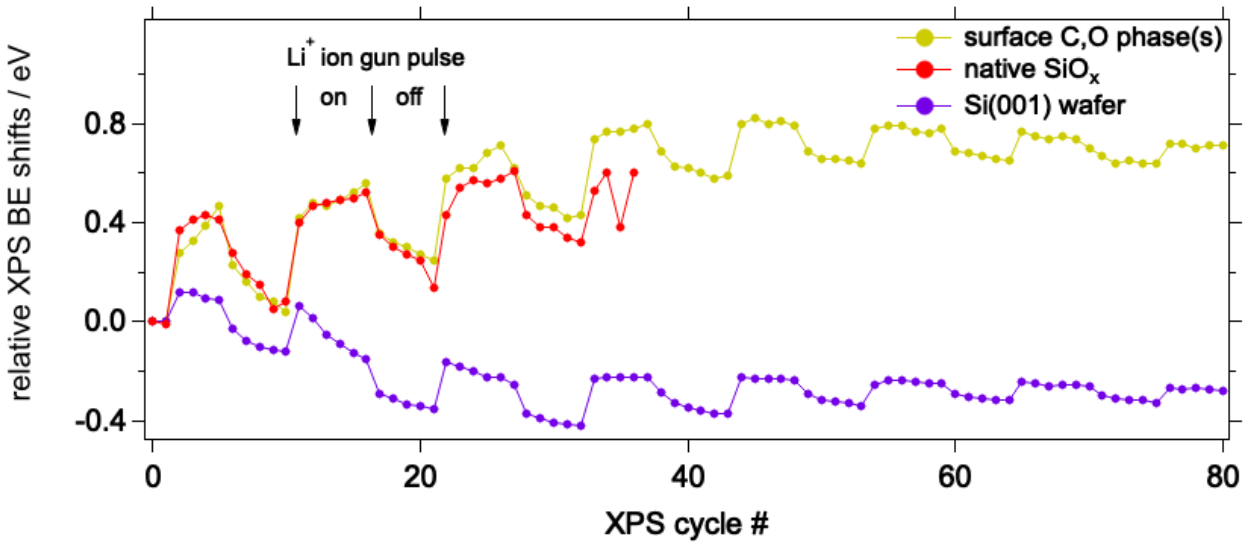
$$Si^0 + xLi^+ + e^- \rightarrow Li_xSi$$

XPS *in-situ* lithiation of native SiO_x/Si(001)

XPS peak areas



XPS peak relative binding-energy shifts

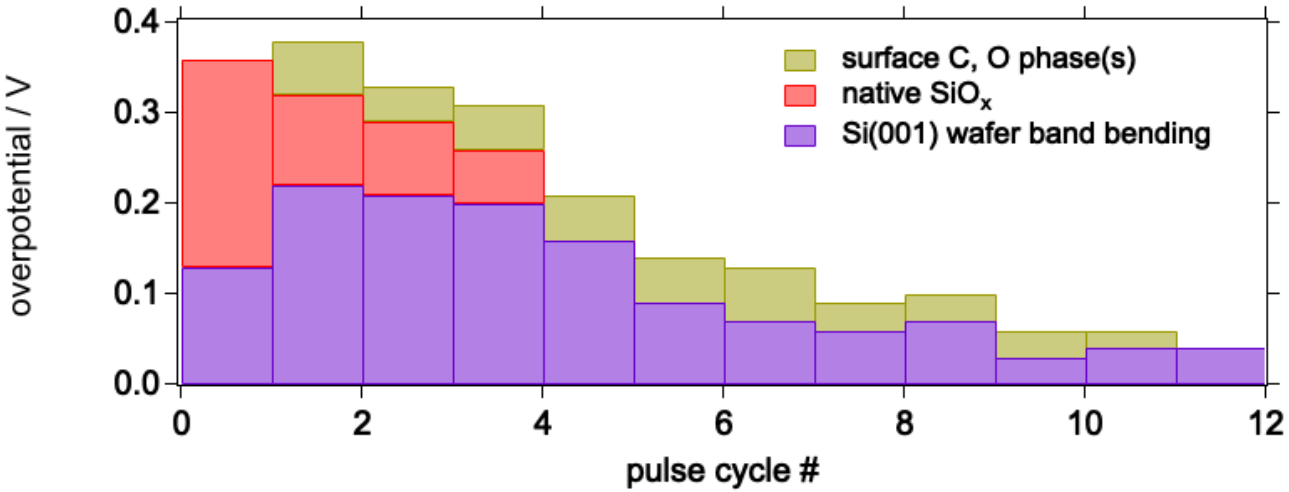


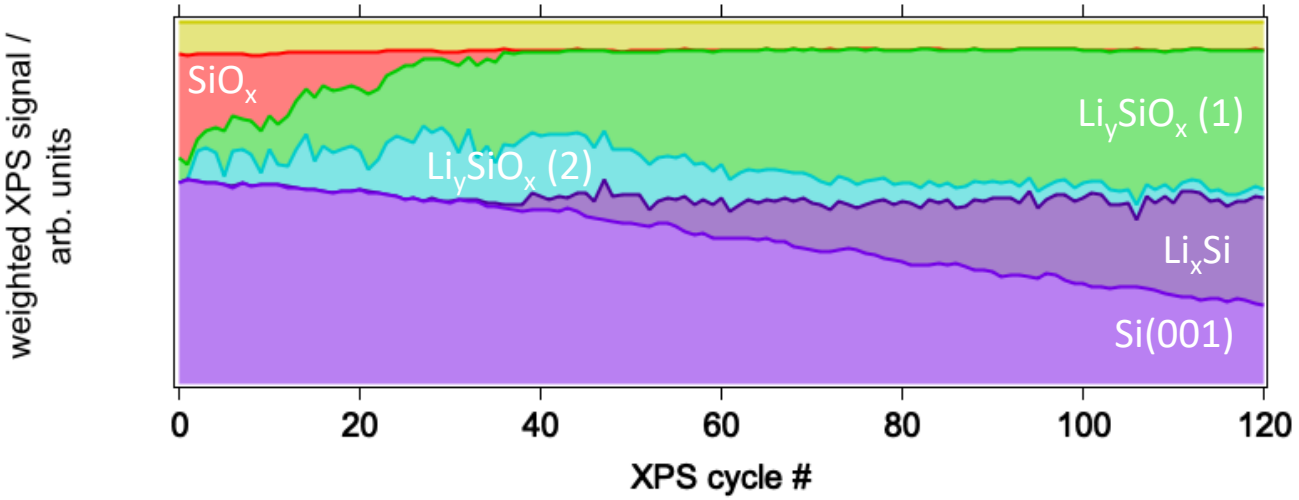
Extraction of chemically-resolved overpotentials:

- Plots of XPS peak areas reveal evolution of phase content within the XPS information depth (~10 nm).
- XPS binding energies exhibit both continuous and abrupt shifts during in situ **pulsed** lithiation:
  - Continuous BE shifts are due to progressive n-type doping Si wafer by Li^+ and changes in SiOx/Si(001) interfacial band alignement.
  - Abrupt shifts results from overpotentials associated with Li^+ migration .

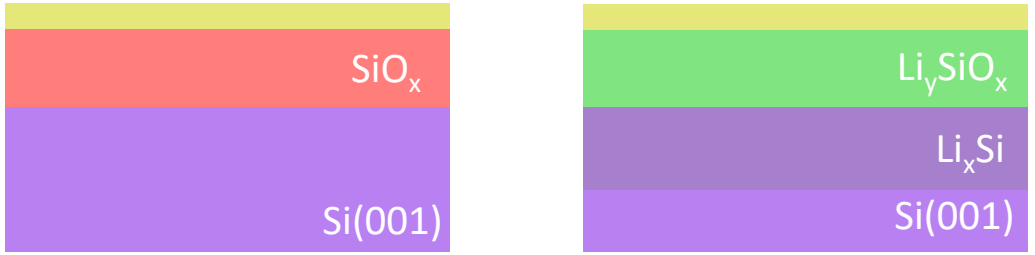
XPS *in-situ* lithiation of native SiO_x/Si(001)

evolution of overpotentials





lithiation



XPS in situ lithiation:

- Chemical-state changes reveal sequential formation of Li_ySiO_x and Li_xSi phases:

$SiO_x + yLi^+ + e^- \rightarrow Li_ySiO_x$

$Si^0 + xLi^+ + e^- \rightarrow Li_xSi$

- Initially both Si(001) band bending and SiO_x layer make substantial contributions to lithiation overpotential.
- At later times uniform n-type doping of Si(001) near the surface flattens bands.

Conclusions

SEISta researchers are developing and applying a range of advanced characterization approaches to elucidate fundamental processes at silicon/electrolyte interfaces, including:

- in situ Neutron Reflectomtery: determinations of SEI thickness and composition of sputter-deposited thin-film a-Si during cycling.
- in situ Surface-Enhanced Raman Spectroscopy (SERS): Raman spectroscopy on realistic anode materials during cell cycling.
- MALDI-TOF-MS coupled with on-electrode Chromatography: detailed studies of electrolyte decomposition products.
- in situ Near-Field FTIR and AFM: coupled nm-scale spectroscopy and topographical measurements during electrochemical cycling.
- Scanning Spreading Resistance Microscopy (SSRM): 2D nanoscale imaging of transport resistivity of battery anode materials.
- Operando X-ray Photoelectron Spectroscopy (opXPS): Simultaneous measurements of changes in composition, chemical states, and chemically resolved overpotentials during cycling of model anodes.

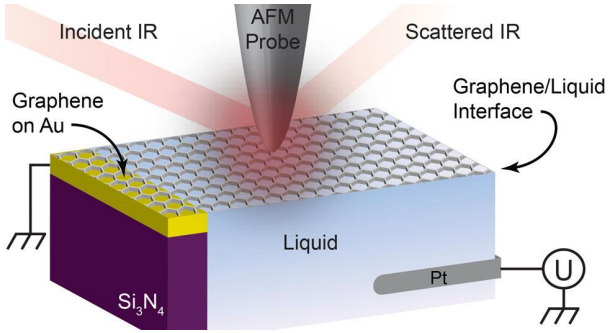
Future work*

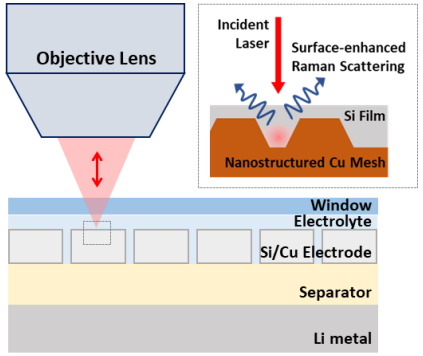
- Continued emphasis on
  - in situ and operando methodologies
  - air-free sample transfer capabilities for routine characterization
  - development and standardization of best practices for data acquisition, analysis and interpretation

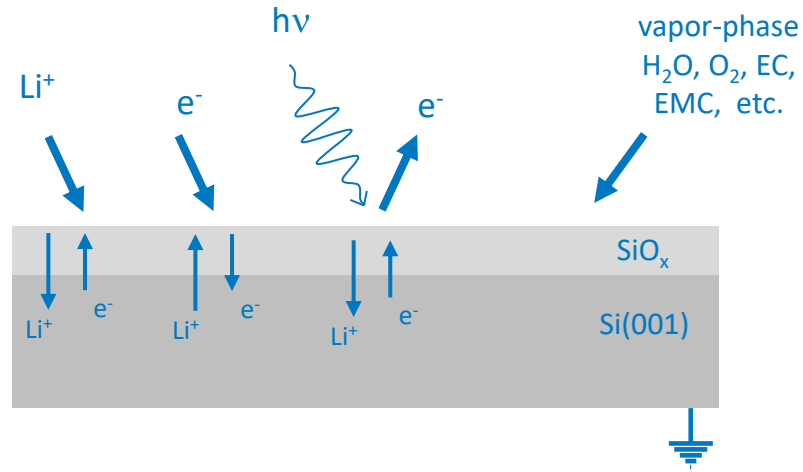
- Future studies on model systems will continue where they can provide clear answers to key questions.

- Effort will also be devoted to applying advanced characterization approaches to “real-world” samples (e.g. CAMP electrodes, Si NP-based anodes, opXPS measurements on organic SEI constituents, etc.)

*Proposed future work is subject to change based on funding levels.







CONTRIBUTORS AND ACKNOWLEDGMENT

Support for this work from the Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Brian Cunningham, Steven Boyd, and David Howell

Adam Tornheim
Alexander Rogers
Alison Dunlop
Andrew Colclasure
Andrew Jansen
Andrew Norman
Andriy Zakutayev
Annalise Maughan
Baris Key
Bertrand Tremolet
Beth Armstrong
Brian Cunningham
Caleb Stetson
Charlie Nguyen
Chelsea Cates
Chen Fang
Chen Liao
Christopher Apblett
Christopher Johnson
Chun Sheng Jiang
Claus Daniel
Daniel Abraham
David Hoelzer
Dennis Dees
Elisabetta Arca
Eric Allcorn
Eric Sivonxay
Fernando Urias-Cordero
Fulya Dogan
Gabriel Veith
Gao Liu
Glenn Teeter
Greg Pach
Guang Yang
Haiyan Croft
Harvey Guthrey
Hetal Patel
Insun Yoon
Ira Bloom
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Jack Vaughey
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Mowafak Al-Jassim
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Sujoing Chae
Tingzheng Hou
Trevor Martin
Vincenzo LaSalvia
Wade Braunecker
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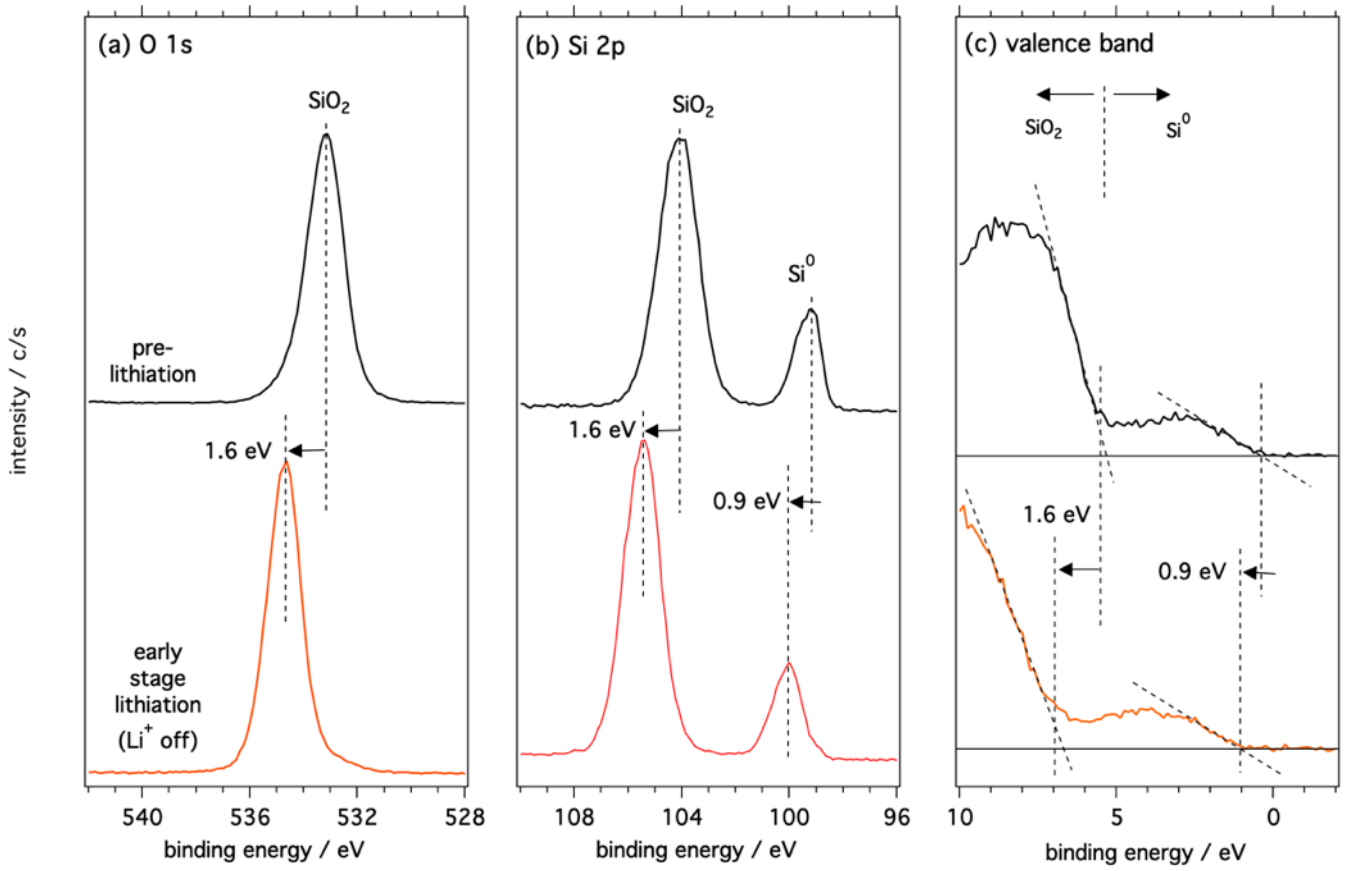
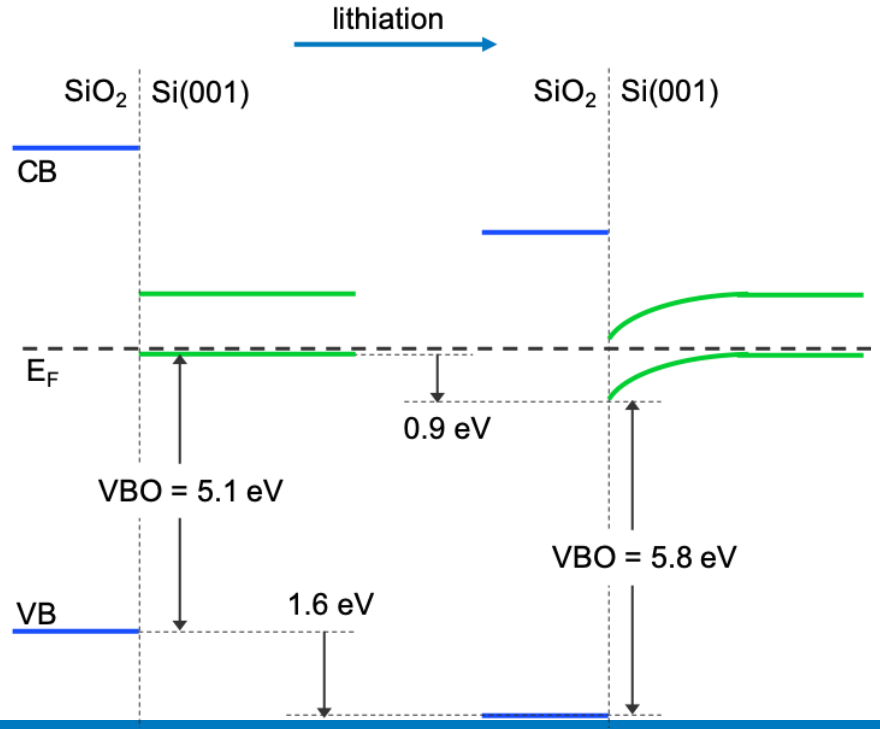
Technical Backup Slides

Pulsed operando XPS lithiation: 5-nm SiO_2/Si(001)



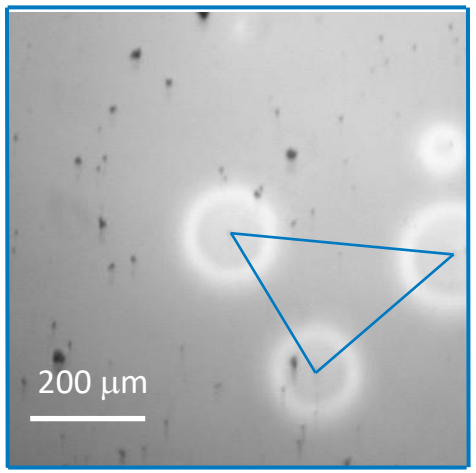
Effects of Li^+ exposure on SiO_2/Si(001) valence-band offset

- after ~ 50 min lithiation O 1s and Si 2p SiO_2 core levels shift to higher bonding energies by 1.6 eV.
- Si^0 core level shifts by 0.9 eV.
- Si^0 and SiO_2 VB onsets shift accordingly, consistent with 0.7 eV change in valence-band offset.



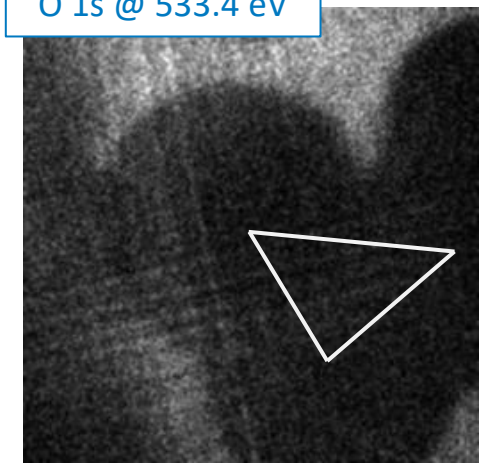
XPS of lithiated 5-nm SiO_2/Si wafer sample: evidence that Li diffuses from the pinhole center

optical micrograph

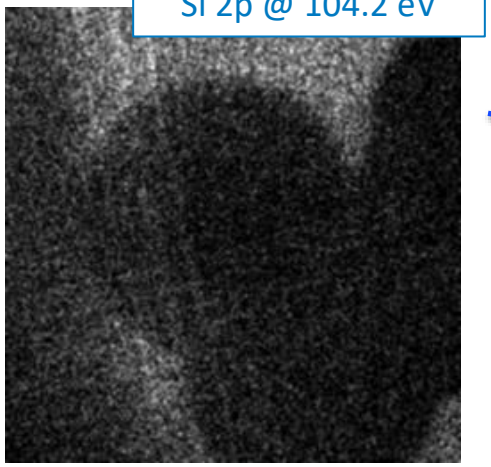


XPS images

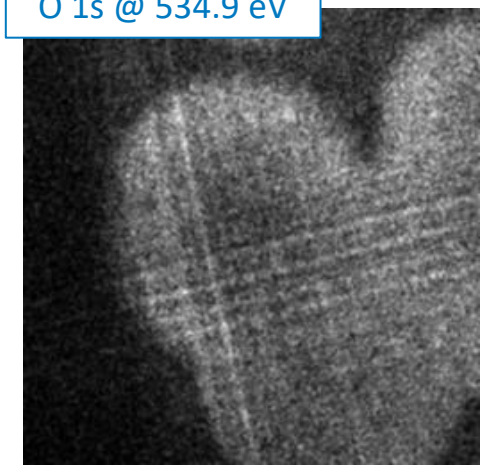
O 1s @ 533.4 eV



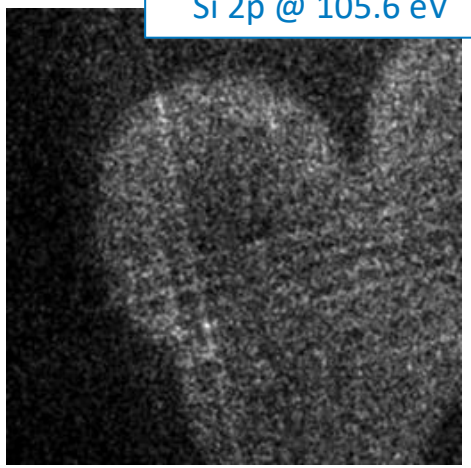
Si 2p @ 104.2 eV



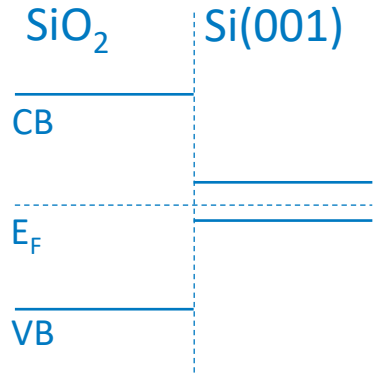
O 1s @ 534.9 eV



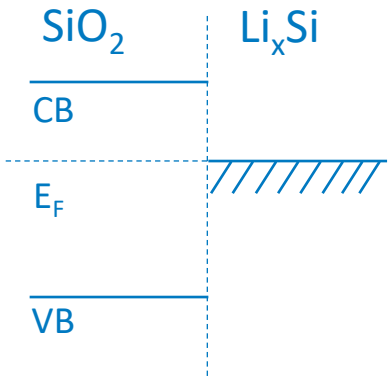
Si 2p @ 105.6 eV



non-lithiated areas w/ no change in band offsets

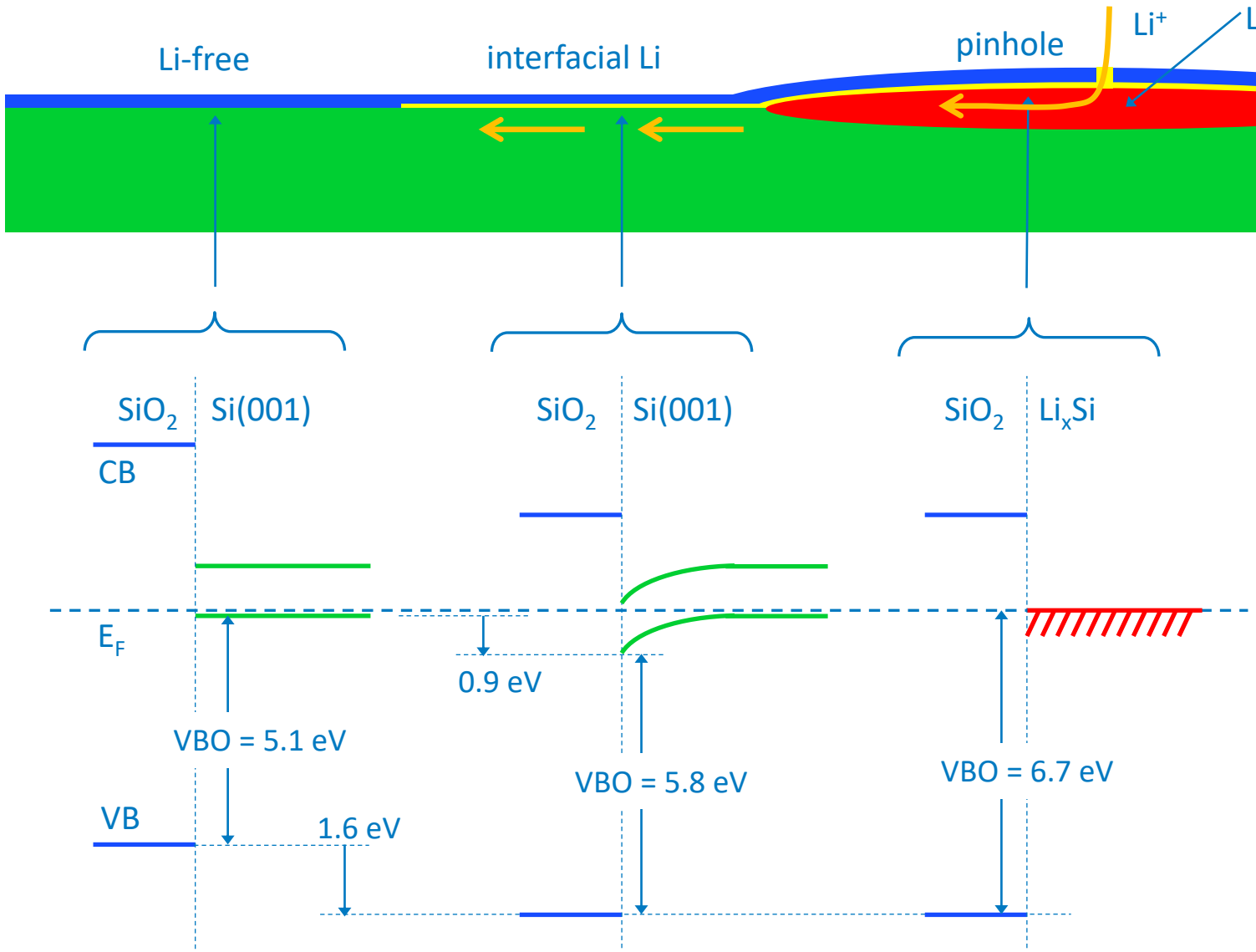


lithiated spots, VBO increases



Regions where SiO_2/Si(001) band-offset has shifted are larger than lithiated spots.

SiO_2 band-alignment with interfacial lithiation from the pinhole



5-nm SiO_2/Si(001) wafer anode

- Lithiation proceeds through channels or pinholes in SiO_2
- Li spreads laterally to form lens-shaped Li_xSi region
- Li^+ migrates preferentially along SiO_2/Si(001) interfaces, alters band alignment

Li is n-type dopant to Si: can locally change doping from p- to n. Band bending = field, may assist Li diffusion